RADIO CORPORATION OF AMERICA
RCA LABORATORIES

Princeton, N.J.
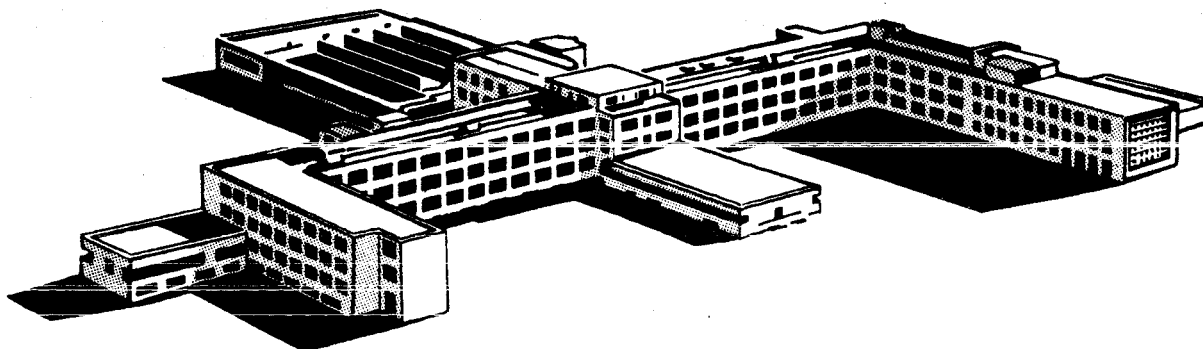
FIRST QUARTERLY REPORT

THIN FILM LARGE AREA
PHOTOVOLTAIC SOLAR ENERGY CONVERTER

REPORT DATE: DECEMBER 31, 1962

CONTRACT NO. NAS7-202

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WESTERN OPERATIONS OFFICE
SANTA MONICA, CALIFORNIA

DAVID SARNOFF RESEARCH CENTER
PRINCETON, NEW JERSEY

FIRST QUARTERLY REPORT

Covering the Period

October 1, 1962 – December 31, 1962

Report Date: December 31, 1962

THIN FILM LARGE AREA
PHOTOVOLTAIC SOLAR ENERGY CONVERTER

(N A S A CONTRACT NO. NAS7-202)
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WESTERN OPERATIONS OFFICE
SANTA MONICA, CALIFORNIA

Work Done By: R. R. Addis, Jr.
S. G. Ellis
W. L. Hui
H. I. Moss
G. Noel
P. Vohl

Report Prepared By: S. G. Ellis
W. L. Hui
H. I. Moss
G. Noel
P. Vohl

Report Edited By: S. G. Ellis, Project Engineer

Report Approved By: P. Rappaport, Project Supervisor

TABLE OF CONTENTS

PURPOSE

The purpose of the program is to investigate materials
and methods for the fabrication of large area solar cells.
The aims of this program are to have efficiencies higher than
5%, areas of the order one foot square, flexible cells, and
relatively inexpensive production costs.

ABSTRACT

Methods are described for the production of n-type and p-type films of gallium arsenide on tungsten and molybdenum sheet. The methods involve the proper choice of source gallium arsenide, ambient atmosphere, substrate preparation and temperature.

An extension of these methods has produced p-n structures in the films, some of which have shown photovoltages as high as 0.3 volts.

Gallium phosphide films have been formed by similar methods, all to-date, have been n-type.

FACTUAL DATA

I. INTRODUCTION AND STATEMENT OF THE PROBLEM

Prior to the commencement of the present contract, work at these Laboratories relating to large area solar cells had fallen into three main catagories: a theoretical evaluation of the suitability of different semiconductor materials; exploratory work on different techniques for film formation; and work on large area CdS cells.

A major conclusion of the theoretical work can be stated: if other factors are equal, the band gaps and optical absorptions of GaAs, InP, and CdTe make them the most prom ising materials for the active elements of large area solar cells.

The following techniques for GaAs film formation were evaluated:

(i) the transport of GaAs down a temperature gradi ent in a sealed evacuated quartz tube, with excess arsenic to maintain an appropriate vapor pressure.

(ii) growth of GaAs films from solution onto various substrates.

(iii) transport by iodine, chlorine, and hydrogen (we now know that the water content of the hydrogen was important) down a temperature gradient in a two zone furnace using a flow system.

(iv) oxide transport in the presence of hydrogen (this method will be described in detail below).

Of these methods the last proved the simplest, quickest and most successful, for use in an experimental program.

The work on large area CdS solar cells[1] gave encouraging efficiencies, particularly if it is recalled that the band gap for CdS is larger than the optimum for matching to the solar energy spectrum. Since this raises the possibility that larger band gap materials may have special merits in a thin film device GaP was added to the list of materials for study.

II. THE METHOD OF FILM FORMATION

The method of film formation now being used was evolved by F. H. Nicoll of these Laboratories. The substrate on which the film is to be formed is positioned near a

1

GaAs "source" crystal, in a furnace containing either dried hydrogen or hydrogen of controlled water content. The source crystal is then heated to a temperature in the range 400°C to 900°C and the substrate to some temperature lower than the source.

There is evidence[2] that gallium is transported to the cooler substrate as an oxide which reduces there:

$$2 \ Ga + H_2O \rightleftharpoons Ga_2O + H_2$$
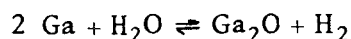
and that arsenic is transported as the vapor.

Two different furnaces have been used in this work. One consists of a 1½" O. D. quartz tube with its center section flattened, Fig. 1. It is closed by neoprene stoppers which are shielded from the hot zone by radiation shields. Heat is provided by one or two Sylvania Type DWY "Sun Gun" Lamps mounted in a semi-cylindrical reflector.

In the other furnace the heater is an electrically heated graphite strip, connected via molybdenum strips to water-cooled posts.

In both furnaces the walls are cooler than the graphite parts. Both furnaces yield films with essentially the same properties.

The hydrogen, supplied from a tank, passes through a train consisting of:

      (i)   needle valve
      (ii) flow meter
     (iii) Drierite
     (iv) a Deoxo unit
      (v) a liquid nitrogen trap

and thence directly to the furnace through a short length of polyethelene tubing if the driest hydrogen is to be used, or through

     (vi) a U tube containing water at 0°C, or 24°C.

After the furnace the gas goes through a bubbler and is vented. When running, the flow rates are of the order 1 ml sec^{-1} or less.

2

Figure 2 shows how the rate of film formation depends on source crystal temperature and water vapor concentration. The film thicknesses are mean values deduced from the weight of the deposits. All points were obtained using the same source crystal. The transfer rate is a function of the orientation of the source crystal. There is a suspicion that the doping agent may also influence the transfer rate.

Attempts to increase the growth rate beyond the values shown in Fig. 2 by the further addition of water vapor failed due to excessive oxidation of the source crystal.

III STRUCTURE OF FILMS

The continuity of the films depends on having a high density of nucleation sites so that the crystals grow into contact while the film is still thin. The density of nucleating sites depends on the substrate, its pre treatment, and its temperature.

The choice of substrates is severely limited by the chemical reactivity of gallium arsenide when hot. The following have been used:

   (i) sheet tungsten, electropolished, either with degreasing
       before use or hydrogen firing at 800°C immediately
       before deposition.
  (ii) sheet molybdenum
 (iii) quartz
 (iv) All of the above, precoated by the vacuum deposition
       of less than 1 micron of germanium at a substrate
       temperature in the range 600°C – 800°C. This greatly
       increases the nucleation density at a given temperature.
  (v) Tungsten or molybdenum precoated by the vacuum
       deposition of less than one micron of manganese
       (at 600°C) or aluminum (at 300°C). These pretreatments
       also yielded a high nucleation density.

In general, as discussed below, the largest GaAs crystals in layers grown on substrates (iv) and (v) had lateral dimensions comparable to the film thickness. The substrate has a doping effect on the GaAs layer This will be discussed in a later section.

Differential thermal contraction between the layer and the tungsten substrate causes the GaAs layer to crack. To date, this has not caused serious difficulties in the electrical measurements. This type of cracking has been reduced by the use of the molybdenum sub strates which provide a better thermal expansion match to GaAs than do tungsten substrates.

3

Several experiments have been conducted with the object of increasing the size of the GaAs crystals. One of these is involved with first increasing the size of the Ge crystals which make up the substrate. A germanium film is evaporated onto a molybdenum strip. This film is alloyed into the surface of the molybdenum at temperatures greater than 1000°C. (The M.P. of the Ge-Mo alloy system continuously rises with increasing Mo concentration.) A second layer of Ge is then evaporated onto the alloy at a substrate temperature around 920°C. The radiation from the evaporation crucible is then enough to form a molten layer of Ge on the surface of the alloy. As the temperature is lowered, the Ge solidifies into elongated crystallites on the order of 1-2 millimeters in extent. It has been possible then to grow GaAs layers whose crystallite size is the same as that of this Ge substrate. (The effect of the increased crystal size on the electrical properties of the films has not yet been evaluated.)

A GaAs film grown on a germanium coated tungsten substrate was examined insitu on an X ray diffractometer. All of the expected reflections were found, indicating no pref erential orientation in the deposit. The lattice constant agreed with that of GaAs to within one part in ten thousand. The $a_1 a_2$ doublet of the incident radiation was resolved indicating good crystallinity. This result, however, tells us very little about the stacking fault and dislocation densities.

GaAs films, more than a few microns thick, grown on germanium coated tungsten substrates have a matted appearance to the unaided eye. A light microscope shows many well developed crystal faces. Some are shown in section in Fig. 3. The lateral extent of these faces is in general comparable in extent to the film thickness. This observation may be explained in the following way: consider the growth of three adjacent crystals 1, 2, 3 of Fig. 4(a). The boundaries between them will not in general be perpendicular to the sub strate. As growth proceeds some of these boundaries meet as at A. The new boundary formed between crystals 1 and 3 will also not in general be perpendicular to the substrate. A continuation of this process leads to the expected structure, Fig. 4(b). It must be remembered that the process goes on in three dimensions so that a crystal nucleated out side the plane of the drawing can grow into it, as at DC.

Prior to the commencement of the contract some thought had been given to methods of manipulating the nucleation process, and some advantages which might accrue as a result.

Suppose that on a conducting substrate which provides ready nucleation for the growth of GaAs we deposit an insulating film containing holes.[†] The holes may be placed

---

† It would be desirable, but is not necessary, that the insulating film provide fewer nucleating sites for GaAs.

at random. Their mean distance apart should approximate, but be somewhat less than the the thickness of the GaAs film to be deposited. The hole diameters should be less than (of the order one-tenth of) the mean interhole distance.

We may expect, Fig. 5, that when the GaAs film has been grown to its terminal thickness, of the many crystals nucleating in each hole only one will grow through to the top surface of the film. Under these conditions the crystal boundaries such as DE which reach the upper surface of the film terminate on the insulating film.

Since we have reasons to believe that intercrystalline boundaries may act as un-desirable conduction paths in a solar cell it will be interesting to see if the above structure can be made, and if it has any superior electrical properties.

IV. DOPING OF GaAs LAYERS

When methods of growing uniform continuous GaAs films had been established attention turned to the control of their conductivity type. This type has been determined by thermal probing, and by the study of the voltage: current characteristics of the film. The observations of conductivity type by these methods have usually been unambiguous and self-consistent.

Experience elsewhere in these Laboratories has shown that the doping of GaAs grown from a vapor phase is a complex phenomena much affected by chemical reactions between the dopant and other chemical species present in the system. Experience with melt doping does not provide a dependable guide on how to proceed.

In the work reported here the following factors influence the conductivity type of the deposit.

      (i)   the doping of the source crystal
     (ii) the substrate temperature during deposition
   (iii) the substrate, and in particular the material added to
            aid nucleation
   (iv) the water vapor concentration in the furnace

At substrate temperatures less than 450°C all deposits were n-type, independent of substrate and source materials. At substrate temperatures in the range 550°C to 700°C a zinc-doped source will give p-type layers on Mn or Ge covered substrates in dry hydrogen. Under these conditions a tellurium-doped source gives n-type layers on germanium coated substrates. While the zinc doped source gave p type layers on germanium covered

5

substrates at the higher temperatures in dry hydrogen, it gave an n type layer if the hydro gen was bubbled through water at room temperature.

Thus it has been possible to deposit n or p type layers at will. The doping con centration and the doping profile in these layers is not known.

V. LAYERS WITH JUNCTIONS

Junction structures have been made by two methods: by changing the source crystal during deposition; and by changing the partial pressure of water during the deposition. This will now be described in more detail.

Using a Mn-on Mo substrates, a p-type film was grown from a zinc-doped source followed by an n-type film from a Se doped source. p-on-n layers were grown using the Ge on-Mo substrate and reversing the above procedure. The layers were tested for con- ductivity type with a thermal probe.

Tin dots, 0.020" in diameter, were pressed to the surface on most of these units to observe diode characteristics on the oscilloscope. A typical curve is shown in Fig. 6. The curves show very little rectification around the origin. Beyond about one volt, the slopes increase in both directions, and show a little rectification. Rough measurements show the series resistance in the forward direction to be of the order of 200 ohms. Using a microscope light under these conditions, open circuit voltages up to 0.35 volts have been generated. These crude measurements indicate that there is excessive leakage in the diode.

In the second method of making a p-n structure a p-type layer was grown from a Zn-doped crystal at 850°C using a germanium-on tungsten substrate and the driest hydro gen. After 20 hours the temperature was lowered to 750°C (so that later the previous growth rate would be restored) and the hydrogen was redirected to bubble through water at room temperature. Growth was continued for another 2 hours. The added water vapor caused an n type layer to form on the previously grown p type layer. At places where the n type layer was sufficiently thin electrical characteristics similar to those described above were observed.

These very preliminary results are on units in which neither the doping, geometry, or connections have been optimized.

6

VI. WORK ON GALLIUM PHOSPHIDE

The performance of single crystal solar cells is not a certain guide to the performance of polycrystalline cells. The inter-crystalline boundaries may degrade the performance is several ways. For example, they may reduce the carrier mobility and hence add series resistance to the cell. They may also provide leakage paths in parallel with the junction.

As mentioned in the introduction, the encouraging performance of large-area CdS cells suggested that in addition to GaAs a higher band-gap material should also be studied, since the crystal boundary effects might then be less adverse. GaP was a natural choice.

GaP layers have been grown by the same techniques used for GaAs, using the type of furnace shown in Fig. 1 and the driest hydrogen. The growth rates, as a function of temperature are shown in Fig. 7.

The substrates used have been tungsten, and germanium-on-tungsten. In both cases good adherence was obtained. The most uniform layers were produced with source temperatures near 1000°C and were n-type for both n-type and p type sources.

CONCLUSIONS

GaAs films, both n-type and p-type can now be produced at will, as well as p-n structures in films. The p-n structures show photovoltages (as high as 0.3 volts), but a performance inferior to single crystal GaAs cells.

The work to date shows several important areas where better understanding is needed: the factors which control the doping of the films, the effect of the inter-crystalline boundaries, and the technology of matching (by electrical connections) these p-n structures to an external load.

Thus, at present, we do not know how to make large area solar cells but we do have hopeful paths to explore.

GaP may prove to be a better material. At present we can make n-type films with it.

FUTURE PLANS

Work will be continued on grown p-n structures and attempts will be made to optimize them. Attempts will be made to produce similar structures by diffusion.

The same structures will be examined in conjunction with the pierced interposed insulator film of Fig. 5 to see if this has advantages.

Single crystal GaAs, one-half covered with Ge or Mn, or single crystal GaAs placed alongside the currently used substrates will be used to compare the electrical properties of single crystal and poly-crystalline deposits, an extension of the technique originally used by Heaps and Pone.[3]

A mass spectrometric study of volatile species produced during the GaAs deposition has just been begun and will be continued.

The central problem, the production of a large area solar cell, would be made much simpler if it were possible to measure the impurity distribution in the structures being made, and also if the electrical properties of the different parts of the structures could be determined.

The standard electrical measurements (resistivity, Hall effect) cannot be made since the films are formed on a conducting substrate. Changing to an insulating substrate may well produce unrecognized changes in the film, since as was seen above the substrate influences the conductivity type, and also the nucleation of the film. In any case such measurements do not separate the crystal, and inter-crystal boundary effects. Nevertheless, as time permits we intend to make electrical (and emission spectrograph) measurements if these have hope of being meaningful.

These conditions limit us to making measurements on more or less completed solar cell structures. In this connection we have begun some exploratory work in which a p-n GaAs structure is compared directly on an oscilloscope with a "simulator circuit" containing a diode, series and shunt resistors and a suitable power source. If the circuit parameters in the simulator circuit can be set so that the simulator gives the same current-voltage characteristic as the experimental cell then we shall have a more quantitative characterization of the cell. This might help in comparing cells and may even indicate ways in which they depart from ideal performance.

The GaP work will continue with attempts to obtain p-type films and then junction structures. In general, the GaP work is expected to parallel the GaAs work.

9

REFERENCES

1. Solar Cell Array Optimization, Contract No. AF33(616)-7415.
    AFD Technical Report 61-11. Vols. I, II and III.

2. C. D. Thurmond and C. J. Frosch, Recent news paper given
    at the Boston meeting of the Electrochemical Society,
    September 1962.

3. Large Area Thin Film Solar Cells, Final Technical Summary
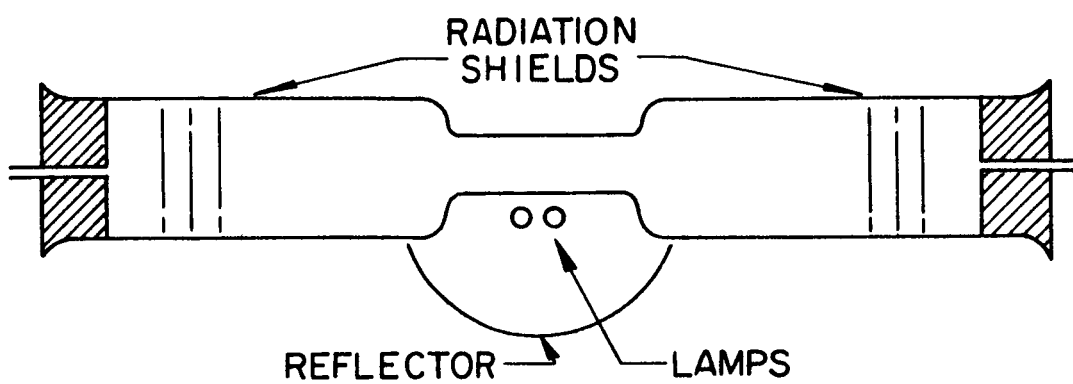   Report. S. C. Contract NO. DA-36-039-sc-88981.
    Task No. 760800061.

RADIATION
SHIELDS

REFLECTOR —— LAMPS

FIG. I

CURVE	CONDITIONS
A	DRIEST HYDROGEN
B	HYDROGEN PASSED THROUGH WATER AT 0°C
C	HYDROGEN PASSED THROUGH WATER AT 23°C

FIG. 2

GALLIUM ARSENIDE
LAYER
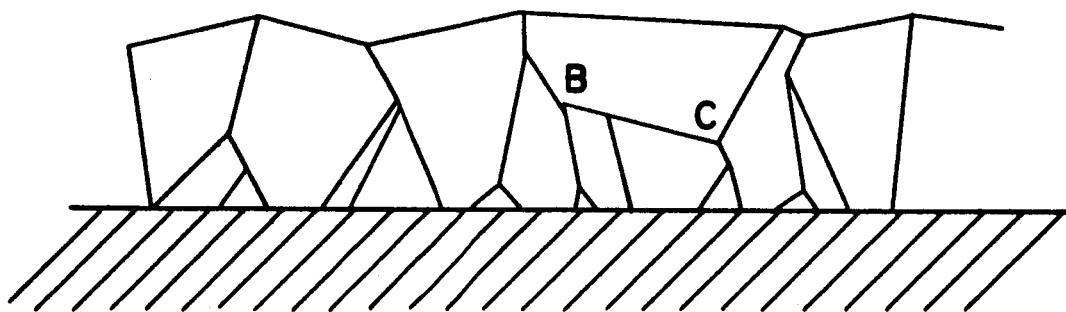
TUNGSTEN
SUBSTRATE

100 MICRONS
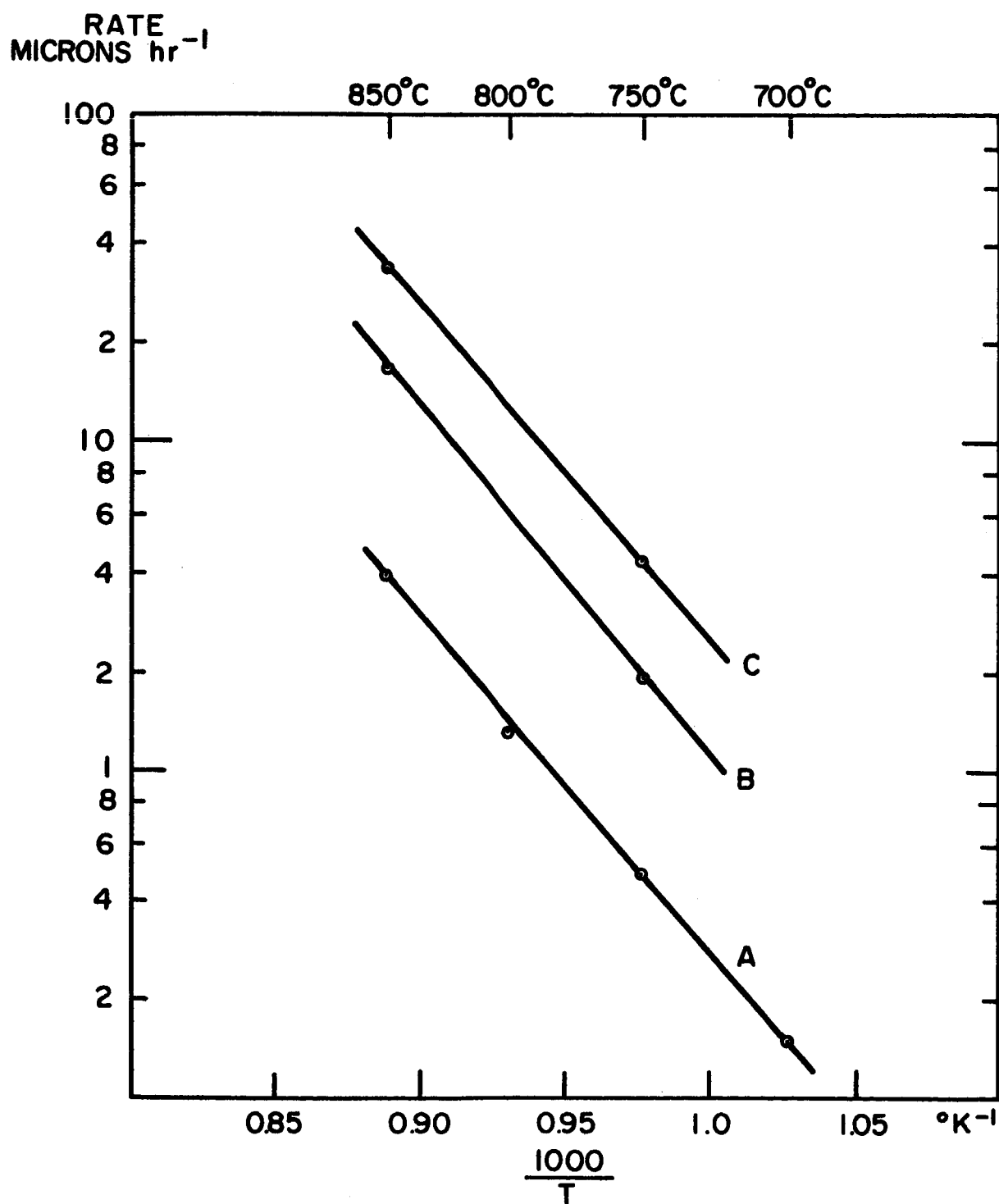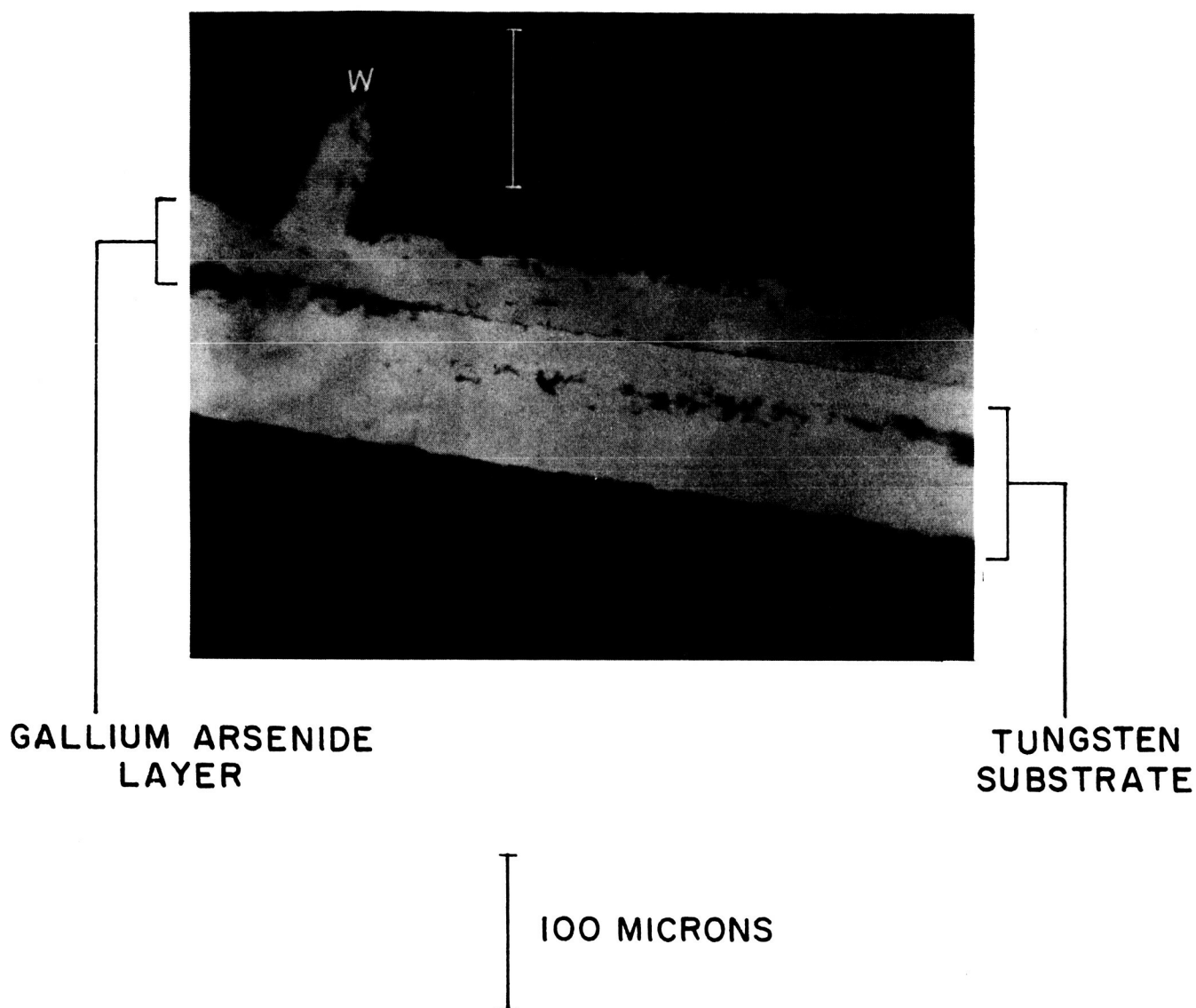
LIGHT MICROGRAPH OF CROSS SECTION OF LAYER.

NOT ETCHED, AND SHOWING DEFECTS IN THE
POLISHING TECHNIQUE.

'W' IS A GaAs WHISKER, AND IS NOT A COMMON
FEATURE OF THE GROWTH
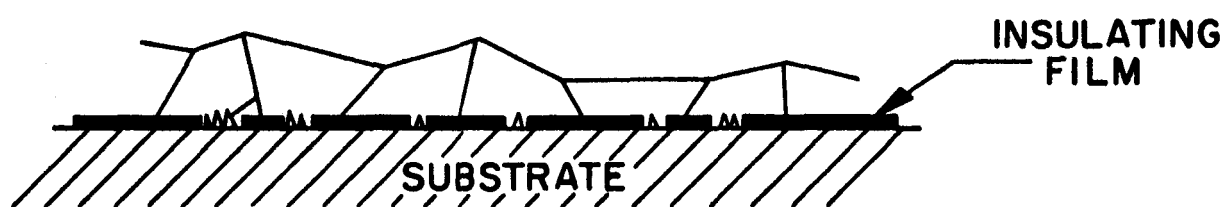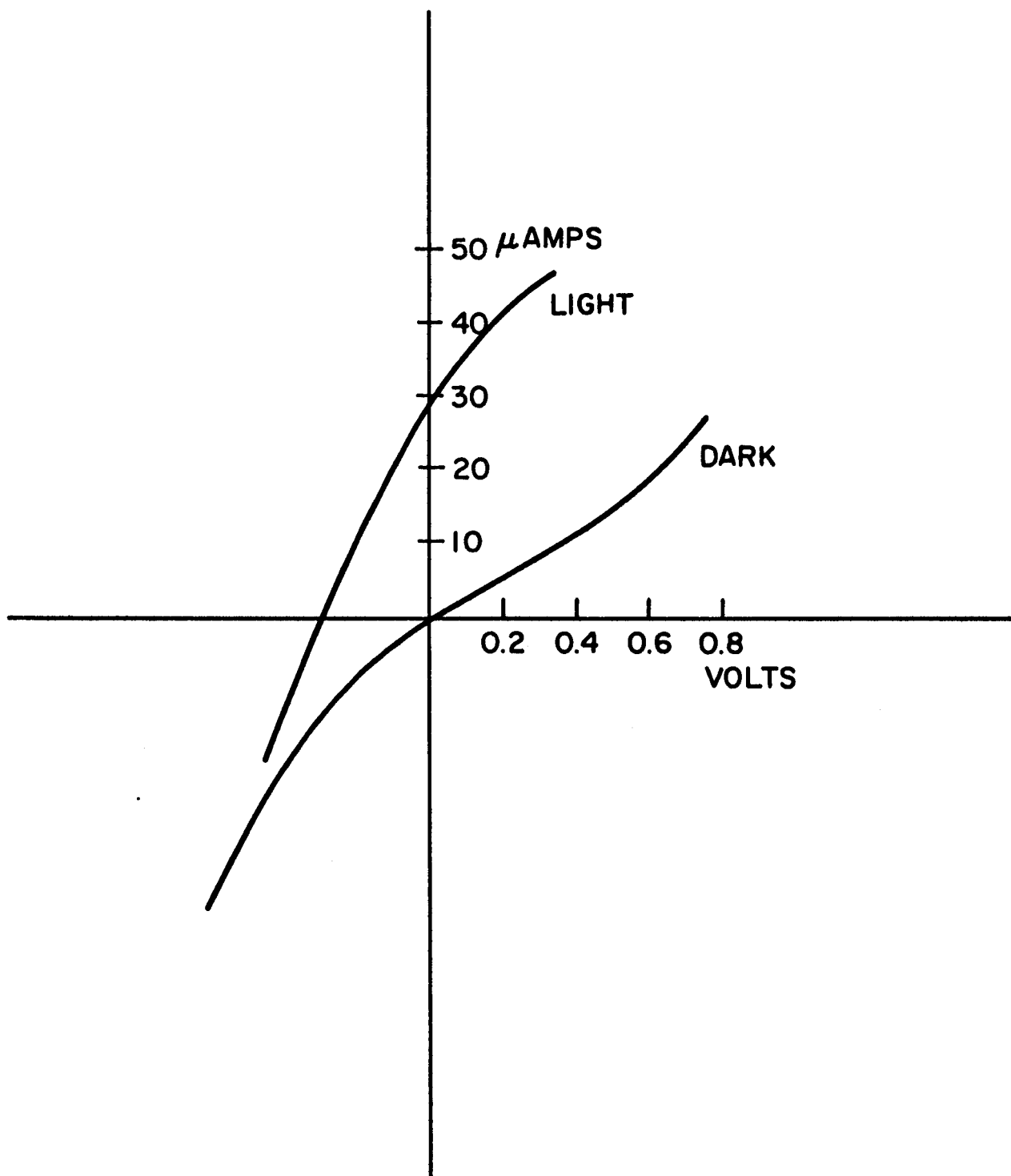
FIG. 3

(a)

(b)

FIG. 4

INSULATING FILM
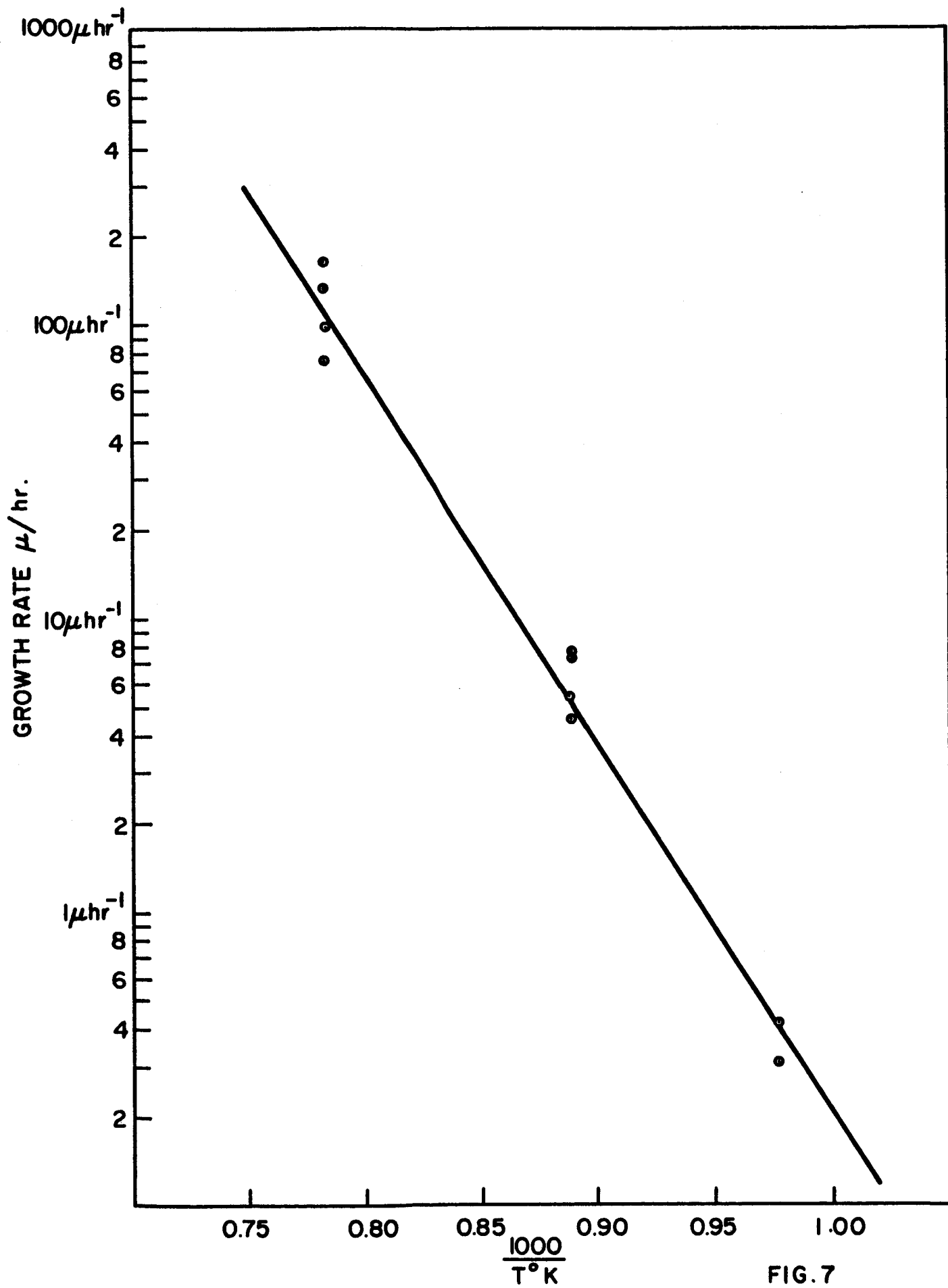
SUBSTRATE

FIG. 5

FIG. 6

FIG. 7